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Advancing Solid-State Interfaces in Li-ion Batteries

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DOE merit review

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Project ID# ES310

This presentation does not contain any proprietary,
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Overview

Timeline

- **Start: November 01 2016**
- **Finish: 2019**
- **15%**

Budget

- **Total project funding**
 - **DOE share: 1500 K**
 - **Contractor 0 K**
- ✓ FY 16: \$ 100 K
- ✓ FY 17: \$ 400 K
- ✓ FY 18: \$ 500 K
- ✓ FY 19: \$ 500 K

Barriers

- **Barriers addressed**
 - ✓ Low conductivity
 - ✓ Interfacial and bulk mechanical and chemical instability
 - ✓ Interfacial ion mobility

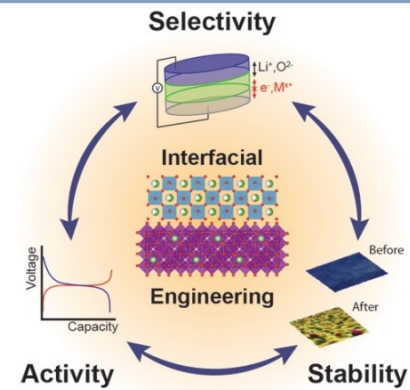
Partners

- **Interactions/collaborations**
 - ✓ Jeff Sakamoto, UM
 - ✓ Amin Salehi (UIC)

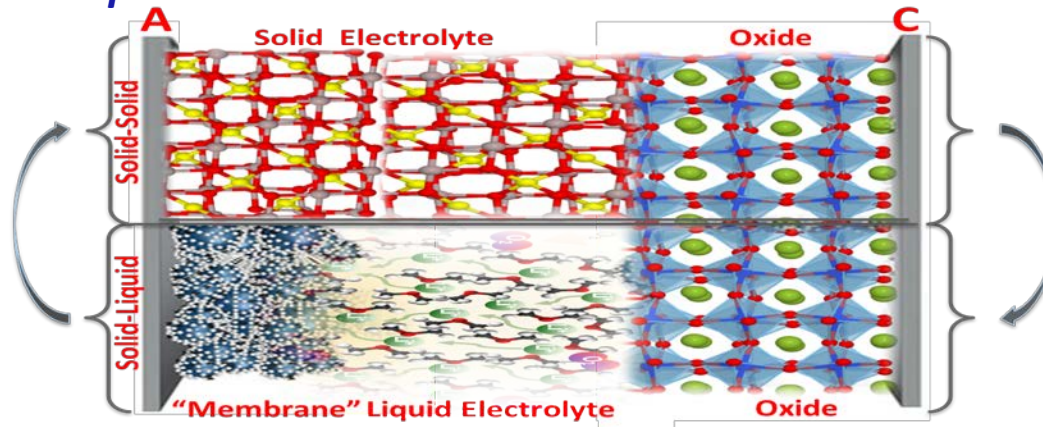
Project Objectives and Relevance

General

Develop and use state of the art experimental and computational techniques to *establish functional links between activity, stability, selectivity and conductivity of electrochemical interfaces and bulk materials in two Li-ion battery systems.*



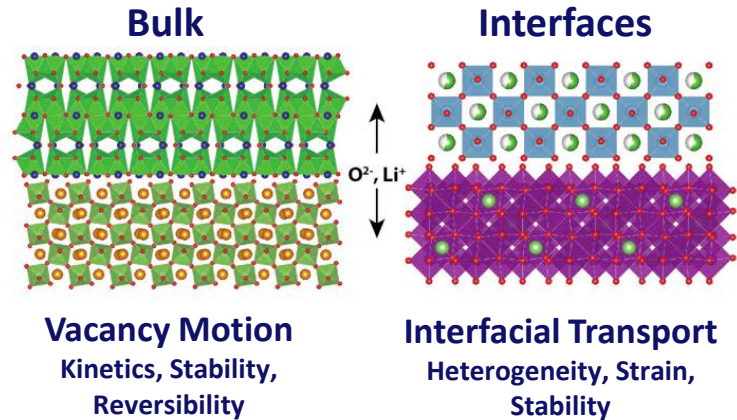
- ✓ **All solid-solid battery (solid electrodes and solid electrolytes - $S_{Li}-S_{EL}-S_{CA}$):** To understand and implement a mechanically/chemically stable and Li ion conductive ($\geq 2 \times 10^{-4} S/cm$ at 298K) nonflammable solid electrolyte capable of protecting a metal Li anode, and that can operate at cathode potentials $> 5V$.



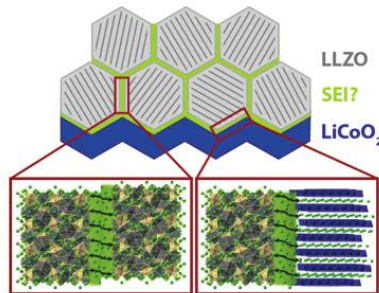
- ✓ **Hybrid solid-solid battery (solid electrodes, “solid membranes” and liquid electrolytes - $S_{Li}-S_M-L_{EL}-S_{CA}$):** To develop a new mechanically and chemically stable Li-selective solid “membrane” capable of protecting the metal Li anode during the discharge process and to monitor stability of cathode materials

Materials and Challenges: $S_{\text{Li}}-S_{\text{EL}}-S_{\text{CE}}$

Bulk and Interfacial properties



Real Systems



“Grain Boundary Transport”
Dendrites, (Electro)chemistry

Moving from model to real systems by precise defect creation

Materials

- Anode interfaces: Li / SrTiO_3 single crystals
- Anode interfaces: Li / $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{M}_{0.5}\text{O}_2$ (M = Nb, Ta)
- Cathode Interfaces: $\text{Li}_x\text{La}_{1-x}\text{TiO}_3$ (LLTO) / LiMnO_2
- Cathode Interfaces: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) / LiFePO_4

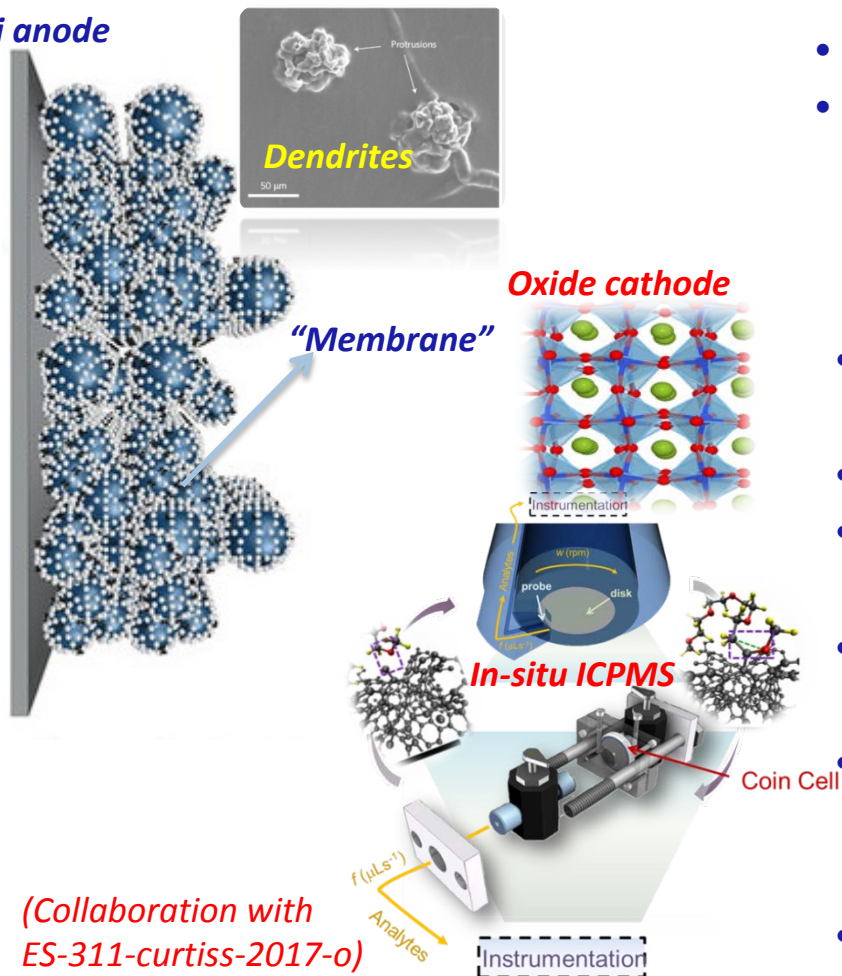
Challenges

- Develop *in situ* probes for exploring interfacial and bulk properties during charge-discharge cycles
- Determine the nature of Li growth on solid electrolytes with controlled defect content
- Define, control and optimize interfacial Li (electro)chemistry as well as interfacial and bulk Li transport
- Optimize interfacial stability and minimize dendrite formation
- Visualize and improve ion transport across buried interfaces using *in situ* X-ray probes at the APS
- Modeling of interfaces to build upon atomic-/molecular-level experimental understanding

Materials and Challenges: $S_{Li}-S_M-L_{EL}-S_{CA}$

Bulk and Interfacial properties

Li anode



(Collaboration with
ES-311-curtiss-2017-o)

**Understanding Li-membrane interfacial
properties and cathode corrosion**

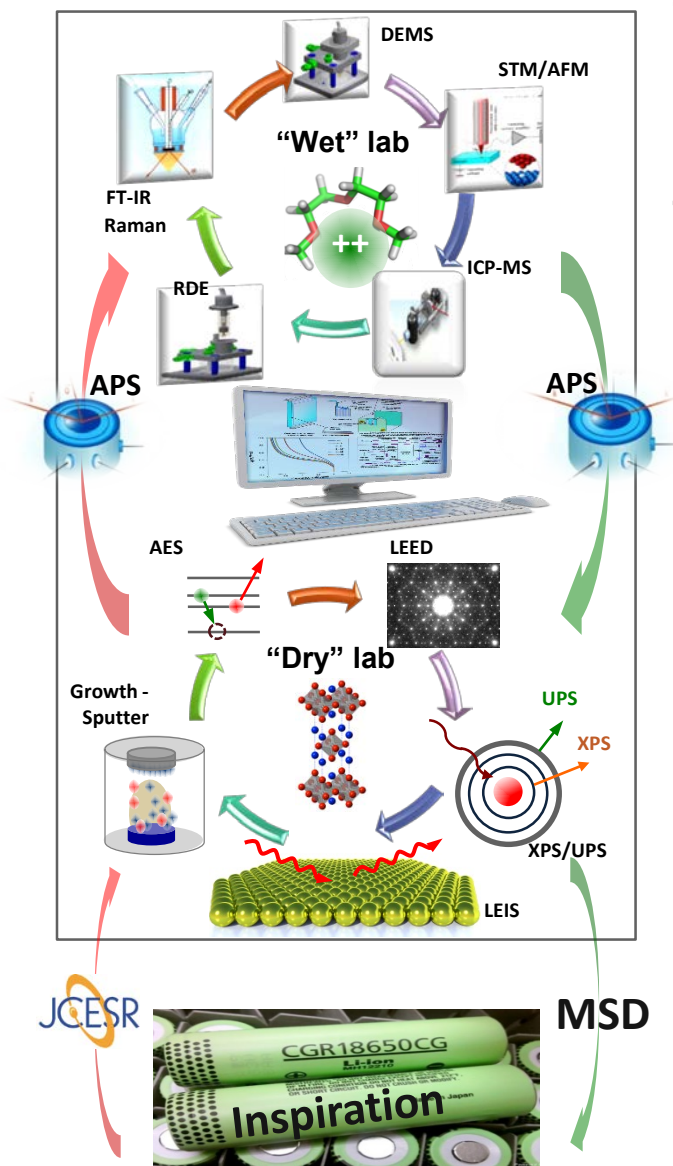
Materials

- Solid-Polymer Protective Membranes
- Lithium Carbonate-based Protective Membranes

Challenges

- Develop membranes that optimize balance between conductivity and thickness
- Enhance liquid electrolyte and electrode stability
- Understand and control dendrite nucleation-growth mechanism at Li-membrane interface
- Demonstrate *in situ* monitoring of dissolution of cathode/laminate components (ICP-MS)
- Develop methods for simultaneous monitoring of corrosion of solid materials (ICP-MS) and liquid electrolytes (DEMS/GS)
- Monitor corrosion of 3d-TM cations and incorporation into protective membrane/anode
- Modeling interfacial and bulk properties

Project Approach



Surface Science-Based Strategy

To define the landscape of parameters (descriptors) that control interfacial/bulk properties for $S_{Li}-S_{EL}-S_{CA}$ and $S_{Li}-S_{M}-L_{EL}-S_{CA}$ Li-ion battery systems. Fast transfer of fundamental knowledge from model to real systems and new challenges from real batteries to model systems

- ✓ Electrode-by-design strategy
- ✓ Electrolyte-by-design strategy

Synthesis Methods

Combination of physical and (electro)chemical approaches

- ✓ Magnetron Sputtering
- ✓ Pulsed Laser Deposition
- ✓ High-Throughput Screening
- ✓ Solid Solution Synthesis
- ✓ Chemical Vapor Deposition
- ✓ Electrochemical Synthesis

Characterization Tools

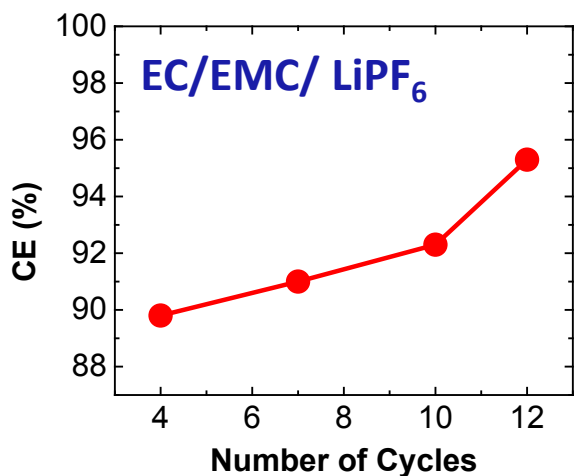
Various *in situ* and *ex situ* experimental probes and first principles-based modeling

- ✓ Low Energy Electron Diffraction
- ✓ X-Ray/Ultraviolet Photoel. Spect.
- ✓ Impedance
- ✓ DFT and Molecular Dynamics
- ✓ Fourier Transform Infrared Spectroscopy
- ✓ Differential Electroch. Mass Spectrometry
- ✓ Scanning Probe Microscopies
- ✓ Soft X-Ray Spectroscopy

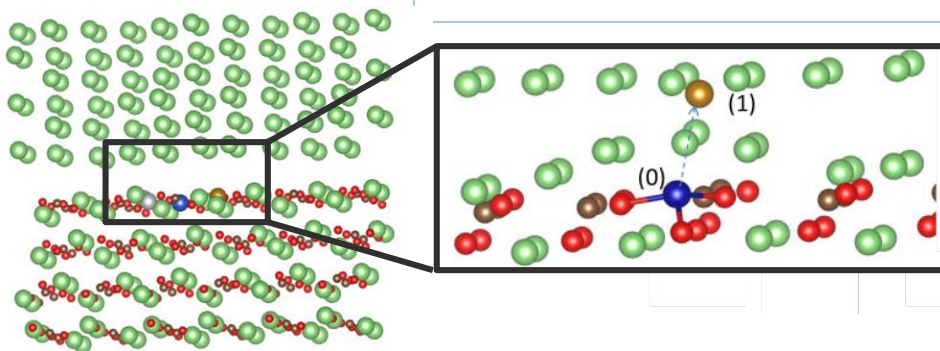
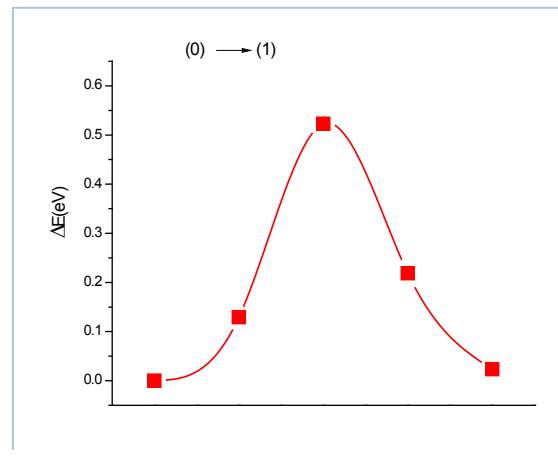
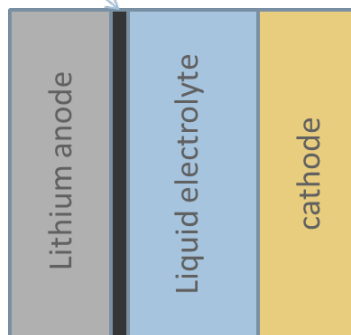
Technical accomplishments: $S_{Li}-S_M-L_{EL}-S_{CA}$

Objective: Use surface science approach to optimize coatings for Li-ion batteries

Works very well in Li-O₂ cells
→ optimize for Li-ion cells

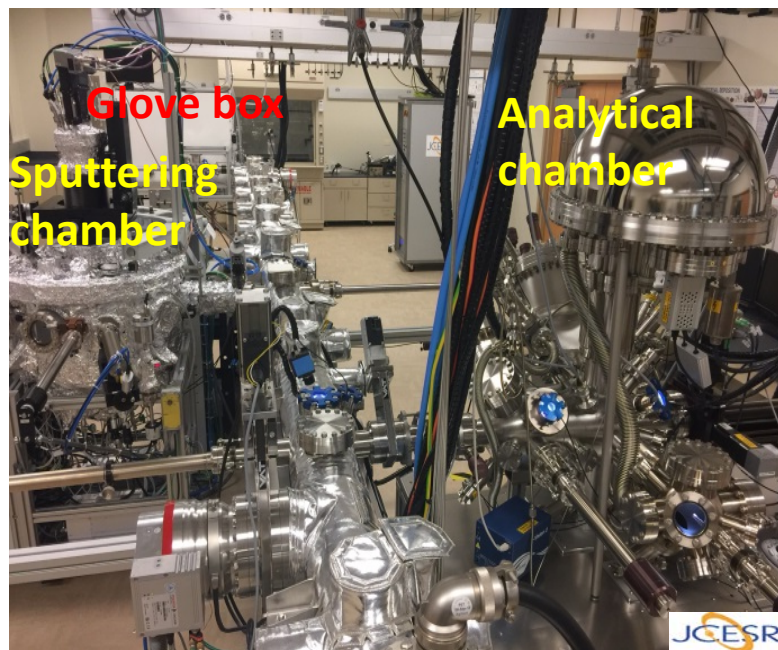
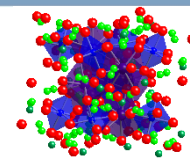
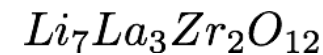


Carbonate coating



Initial results from a standard protocol
lithium anode test: coulombic efficiency
increases with coating thickness

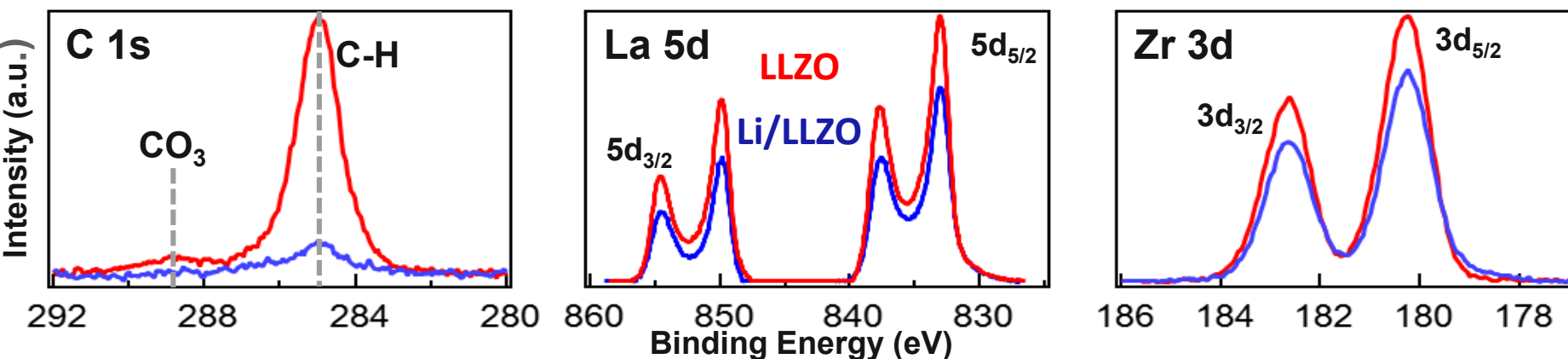
DFT studies of energetics for Li
deposition at a Li/Li₂CO₃ interface



UHV Characterization: fully developed Li sputter deposition/characterization methods (Li on LLZO and perovskite materials)

Battery testing: established protocol for sample transfer from UHV to glove box and back to UHV for post-cycling analysis.

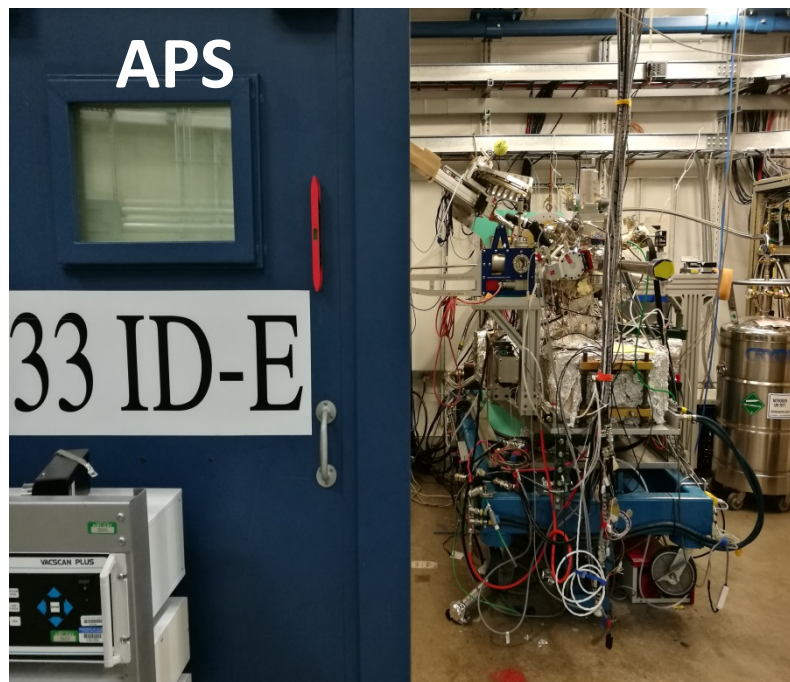
XPS spectra for Al-doped LLZO and Li/LLZO



- Clean surface - no Li_2CO_3
- No changes in surface chemistry upon Li deposition, consistent with expectation that Al-doped LLZO is stable to Li metal

(Collaboration with J. Sakamoto)

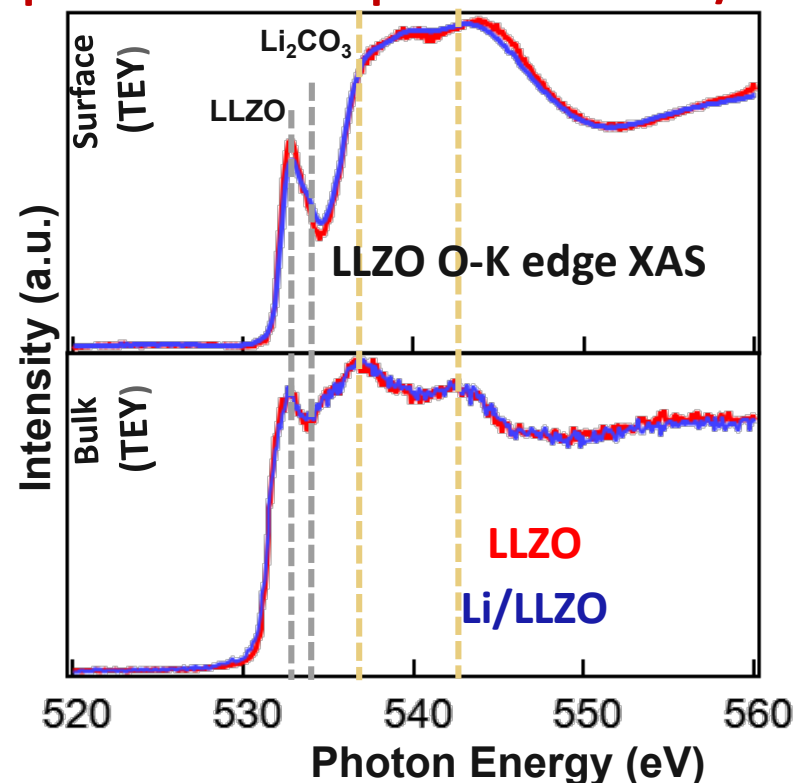
Technical accomplishments: Li/LLZO



XAS Characterization: fully developed Li sputter deposition/characterization methods (Li on LLZO and perovskite materials)

Sample Transfer : established protocol for sample transfer from UHV to APS facilities.

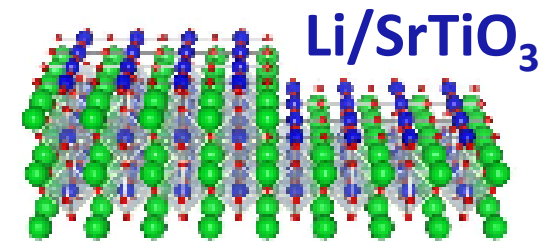
XAS spectra for Al-doped LLZO and Li/LLZO



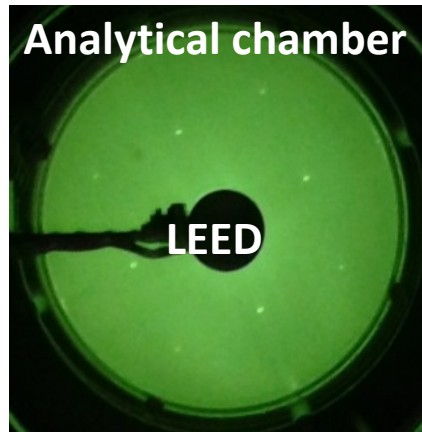
- Surface total electron yield (TEY) spectra indicate surface does not contain a substantial amount of carbonate, consistent with XPS
- Bulk total fluorescence yield (TFY) spectra indicate the bulk is unchanged by Li deposition
- Shift in fine structure peaks unclear

Need well defined interface in order to understand what is going on!

Technical accomplishments – Perovskite systems



Clean STO surface



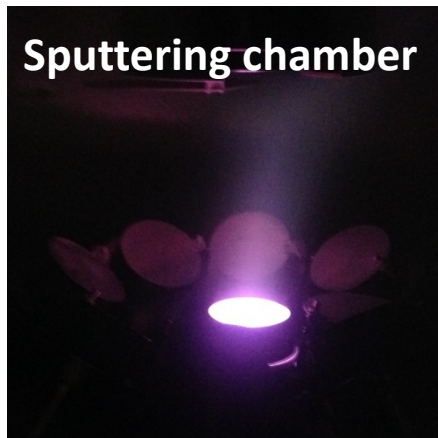
Why SrTiO_3

- Well-ordered with known surface and bulk properties
- Flat surface to stabilize deposited films
- Allows Li interaction with oxygen and cations to be probed at atomic levels

Synthesis of Li interface

- Li sputtering ~ 30 min at 25 and 100°C
- “Rough” Li film (≥ 20 nm islands)

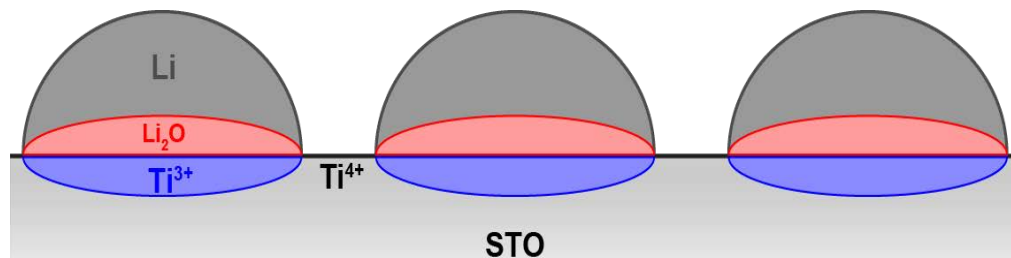
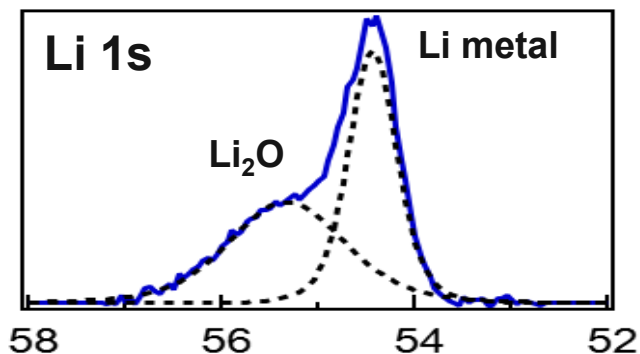
Li-STO surface



UHV characterization

- Low-energy electron diffraction (LEED)
- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)

Chemical stability of Li/STO interfaces



XPS analysis

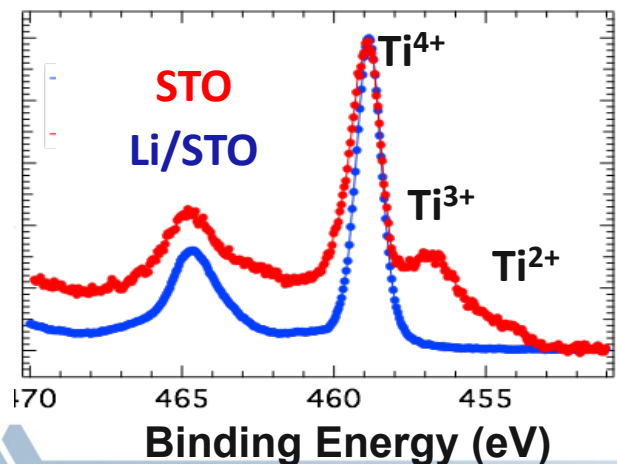
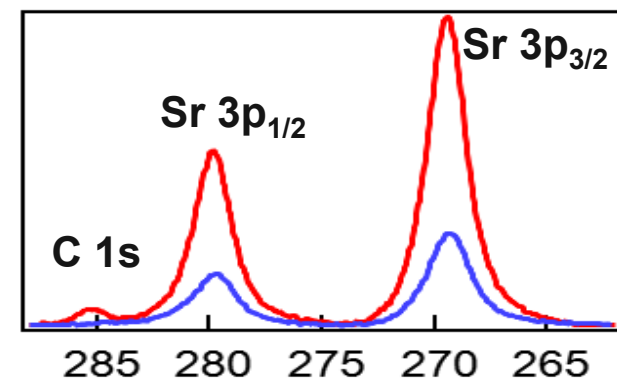
- **Li 1s to track state of Li**
 - ✓ Li metal and Li_2O ; Li interacts with O at interface
- **Sr 3p to track valence state of Sr**
 - ✓ No change in the valence state
- **Ti 2p to track valence state of Ti**
 - ✓ Reduction of Ti^{4+} to Ti^{3+} and Ti^{2+}
 - ✓ Li reacts preferentially with O bonded to Ti

Conclusions:

Li interacts with near-surface O, leading to:

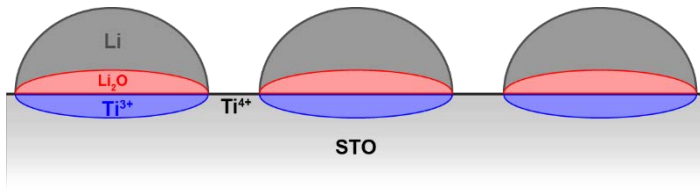
- ✓ Chemical transformations
- ✓ Interfacial instability

Intensity (a.u.)

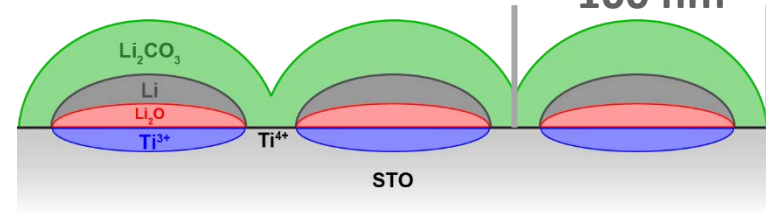


AFM: Li Deposition on Nb-doped STO

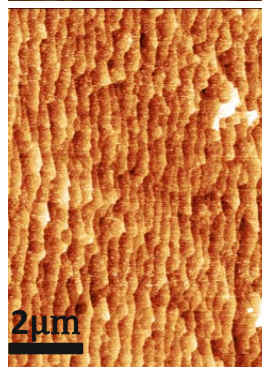
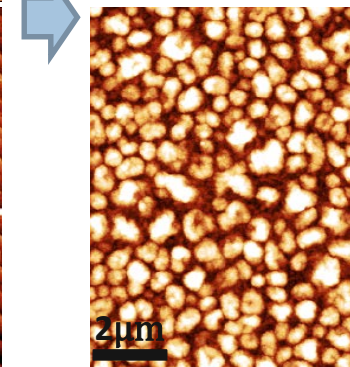
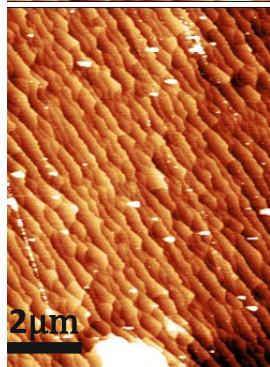
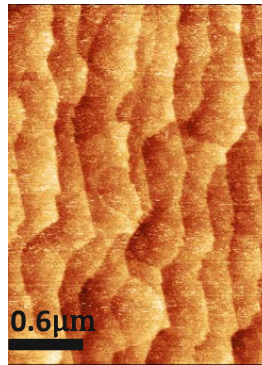
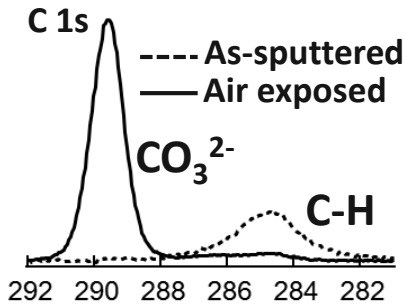
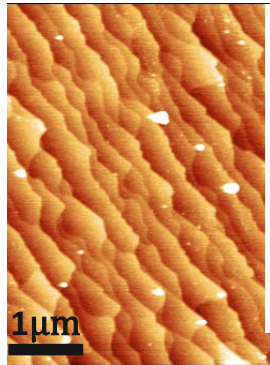
After Li Deposition



After Air Exposure



1. Clean (HF etched) STO 2. Sputtered Li 3. Back to Clean STO



Exposed to air and formation of Li_2CO_3 Ultrasonicated in water ✓ to remove Li_2CO_3

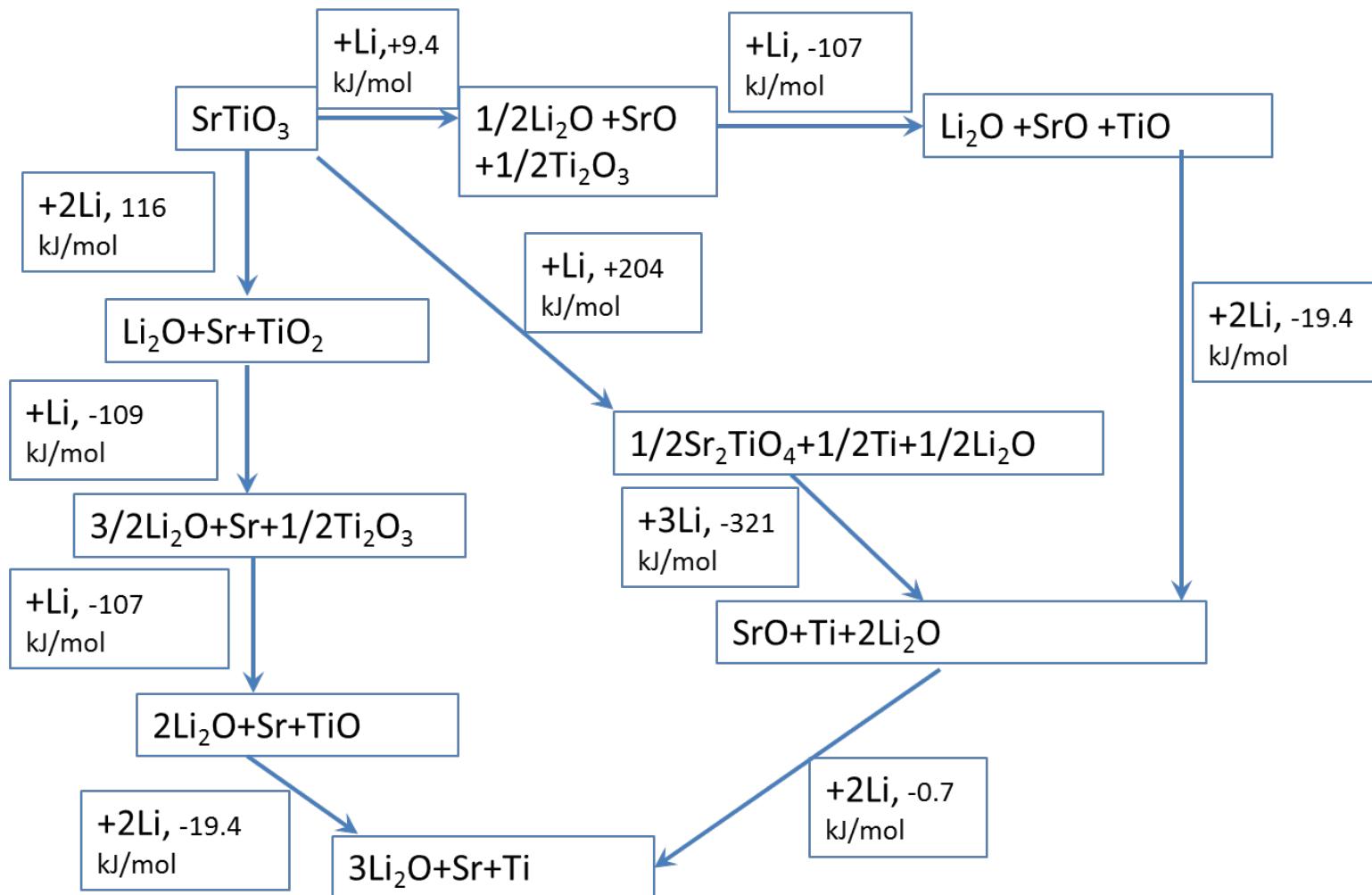
AFM analysis

- Step 1. Clean and ordered terraces
- Step 2. Island structure after Li deposition and exposure to air (Li_2CO_3 formation), consistent with non-conformal deposition of Li at R.T.
- Step 3. Very little modification to surface structure after sonicating sample in H_2O

Conclusions:

Stranski-Krastanov mode of Li deposition (island formation)

Thermodynamics of Li/STO interfaces

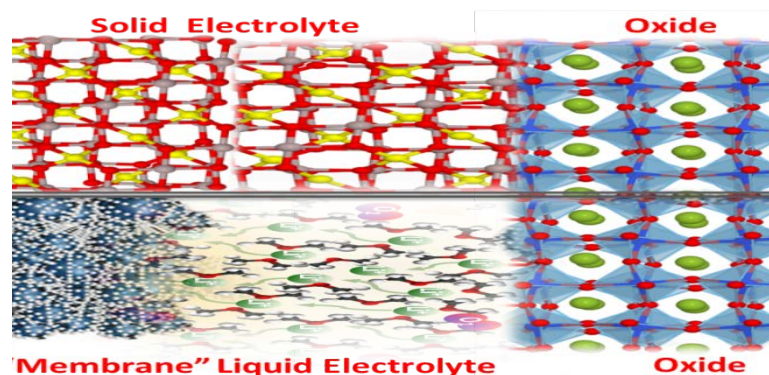


Li causes Ti oxide reduction before Sr oxide

Summary

Developed state-of-the-art experimental and computational techniques for *monitoring Li interaction (chemical stability) with well-characterized LLZO and STO(hkl) substrates*

- ✓ No obvious changes in surface chemistry upon Li deposition, consistent with expectation that Al-doped LLZO is stable to Li metal
- ✓ Some evidence from XAS that there are differences in surface vs. bulk chemistry and/or electronic structure, but the origin of these differences is unclear
- ✓ Li deposition on STO clearly leads to surface reduction of Ti, with no redox on Sr sites
- ✓ Exposure to air results in carbonate formation, which can be removed from surface via sonication in H₂O
- ✓ Surface redox does not result in dramatic changes to surface morphology (only small increase in RMS surface roughness)



- ✓ Successful tuning of Li₂CO₃ thickness for improved cyclability in EC/DMS electrolytes

Milestones

Month/Year	Milestones
Dec 16	Developed UHV synthesis and characterization methods for controlled deposition of Li on STO single crystals. Completed
Mar 17	Coupled UHV-based experimental techniques and computational methods for elucidating parameters that control the interaction of Li anode with individual components of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{M}_{0.5}\text{O}_{12}$ (M = Nb, Ta) and Li_2CO_3 “membrane” On schedule
Jun 17	Design and develop <i>in situ</i> evaluation of stability of both Li_2CO_3 “membrane” (ICP-MS) and gas evolution from selected organic electrolytes during charge-discharge processes (DEMS) On schedule
Sep 17	Investigate the coulombic efficiency of, as well as the charge-discharge cyclability for, $\text{S}_{\text{Li}}\text{-S}_{\text{EL}}\text{-S}_{\text{C}}$ and $\text{S}_{\text{Li}}\text{-S}_{\text{M}}\text{-L}_{\text{EL}}\text{-S}_{\text{C}}$ systems On schedule

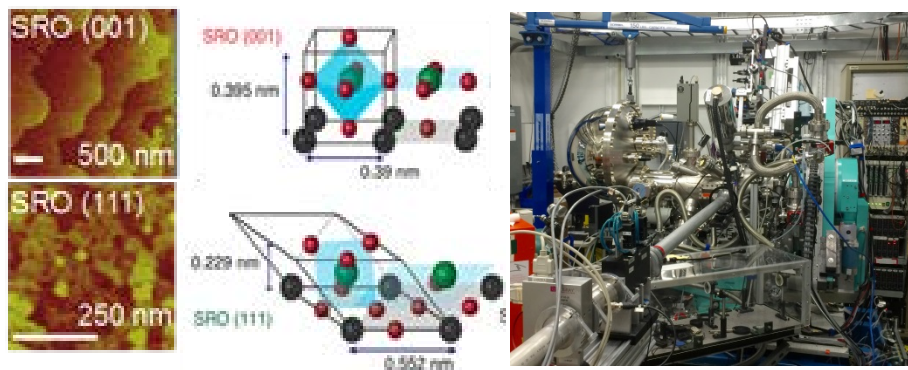


Research plan and future directions

(Experimental synthesis and characterization methods)

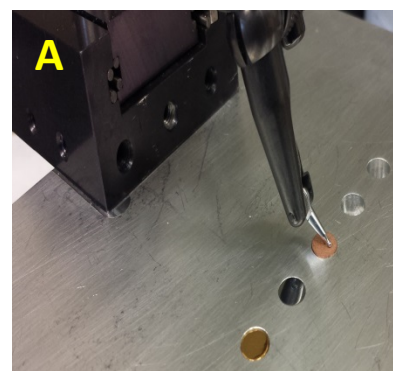
Development of new physical synthesis and characterization methods for controlled deposition of lithium on selected membrane and solid electrolyte materials

PLD-X-ray Scattering-HAXPES System



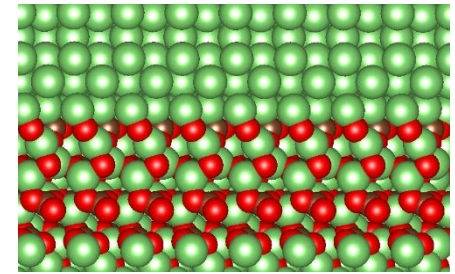
- Develop PLD method for synthesis of well-defined solid-solid interfaces
- Design and develop multimodal sample holder for electrode transfer from MSD to APS
- APS: *in situ* XPS and XANES measurements
- Connect UHV and impedance spectroscopy measurements

Development of *in situ* (electro)chemical characterization methods for probing stability, selectivity and activity of interfaces in a coin cell format



- Design and develop coating methods
- Design and develop simultaneous evaluation of electrode material corrosion (ICP-MS) and electrolyte decomposition (DEMS)





Hybrid systems:

- Investigate the coulombic efficiency and the charge-discharge cyclability in full Li-ion cells
- Optimize the thickness/composition of the protective layer
- *In situ* monitoring of the stability of electrode materials and electrolytes
- Explore morphological and chemical properties of the protective layer
- Introduce computational methods to understand interfacial properties and optimize the coating properties

Any future work is subject to change based on funding levels

Research plan and future directions

Solid-solid systems:

- Ion transport through the bulk and across heterogeneous interfaces.
- The role of strain (coherent XRD) and vacancy mobility.
- The role of doping elements on interfacial properties
- Stability of Li-electrolyte interfaces (chemical and mechanical)
- More emphasis on understanding interfacial properties of cathode-electrolyte interfaces.
- Fast transition from well-characterized epitaxial films to real systems

Any future work is subject to change based on funding levels



- Anode interfaces: Li / $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{M}_{0.5}\text{O}_2$ (M = Nb, Ta)
- Anode Interfaces: Li / $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$

DOE

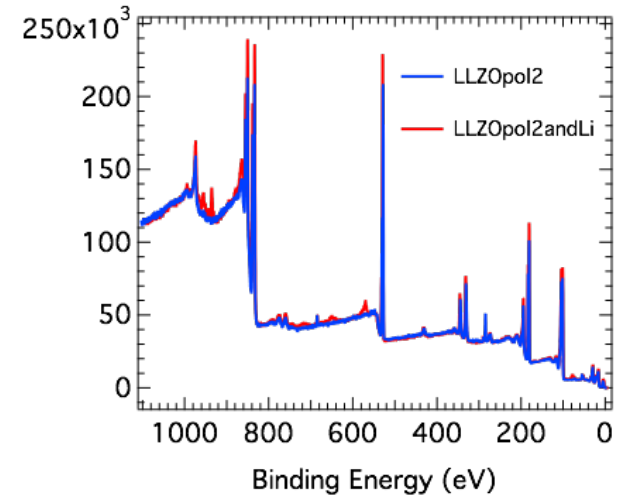
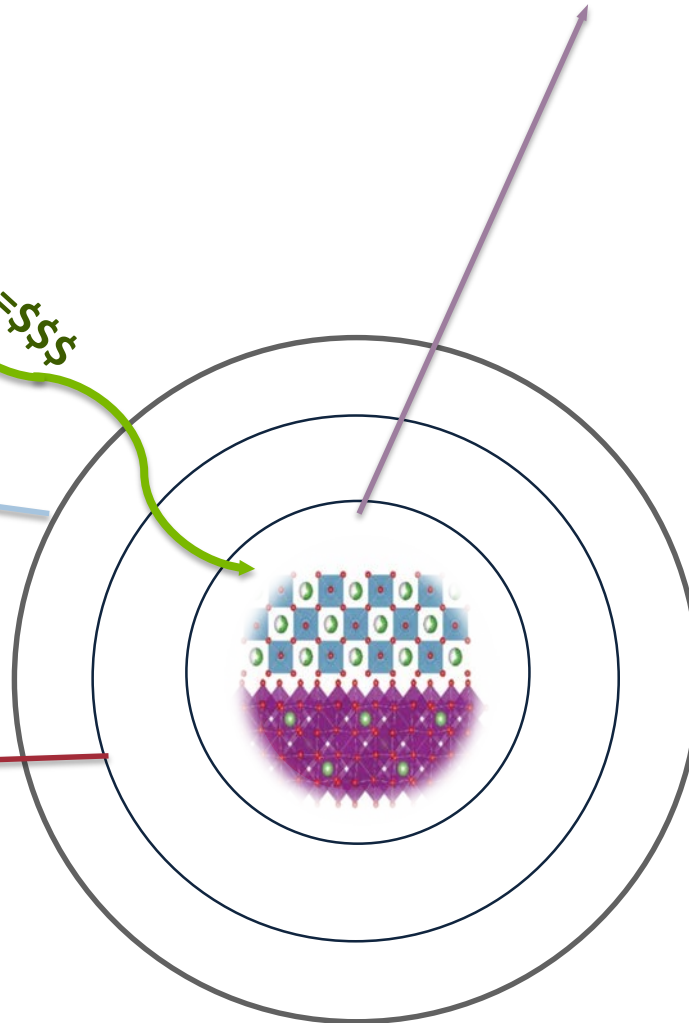
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MSD (Synthesis)

- John Mitchell
- Mercouri Kanatzidis

Toyota (possible)

- Anode interfaces:
Li / $\text{Li}_2\text{S-P}_2\text{S}_5$



Lithium (1s): 60-50 eV

Carbon (1s): 290-280 eV

Oxygen (1s): 540-520 eV

Lanthanum(5d): 860-830 eV

Zirconium (3p) : 540-520 eV

**This project is a new start and
no comments from 2015 AMR are available**